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From: David Tsui <tsuid@FALCON.AL.WPAFB.AF.MIL>
To: RTP7.RTPECAO(JARABEK-ANNIE),CIERC02.CIRREL1(URBANS...
Date: 7/17/98 10:19am
Subject: Re: Perchlorate -Forwarded

per A.J.

To all,

Re: Oxidizing potential of perchlorate under physiological conditions

Where do I begin?...Here is the short answer...
Don't bother looking for perchlorate metablites in-vivo. Perchlorate is unlikely to get reduced at physiological conditions.

If you are looking for punishment, here is the long answer...
The thermodyanic tendency of the halogen oxoanions and oxoacids to participate in redox rxns is well understood. Reduction potentials (E) for oxoanions increases with respect to their oxidation number. For chloro-oxoanions, the reduction potentials is in the order of Cl2< HOCl< HClO2-< ClO3- <ClO4-. The reduction potentials for oxoanions in basic solution is lower when compared to acid solution. At pH=0, the reduction potential of perchlorate to chlorate and water is 1.20 V, and at pH=14, reduction potential of perchlorate to chlorate and hydroxide is 0.37 V. Thermodynamically, perchlorate is a stronger oxidant in the chloro-oxoanion series at the extremes of the pH scale which are difficult to achieve in-vivo. Perchlorate ion is one of most stable oxychlorine compounds. When chemists said that perchlorate is a powerful oxidant they mean the amount of free energy (G) released during a rxn. Since G= - nFE, negative G means the rxn is thermodynamically spontaneous,...and the reduction potential of perchlorate is very very high,...

The rates of halogen oxoanions redox rxns are difficult to rationalize. However, the experiementally observed trend is that the rate becomes faster as the oxidation number of the halogen decreases. For chloro-oxoanions, the oberved rates are in the order: ClO4- < ClO3- < ClO2- < ClO-. It has been theorized that the rate of redox rxn is controlled by the rate-limiting halogen-oxygen bond scission. Thus group VII (halogen) oxoanions, which have the shortest and the strongest bonds of all the oxoanions, are the least reactive. Halogn-oxygen bond scission can be approximated by the rates of oxygen atom exchange with water and perchlorate ions do not exchange their oxygen atoms with water at a measurable rate. Relatively speaking, it is very, very, very, very, very, very slow. The reduction rate of perchlorate is second-order in [H+] and proportional to [reducer]. In the absence of free H+ as in-vivo, a reducer or a catalyst with "oodles" of free potential energy is needed to increase the rate, and I don't know if they exist in-vivo. Probably not.

Let me know if you have any questions. Have a nice weekend!

>>> ANNIE JARABEK <JARABEK.ANNIE@epamail.epa.gov> 07/16 9:35 AM >>>
Guys,

This is being raised by the genetox reviewer on the assessment team.

I
am not convinced that perchlorate is an oxidizer even in vivo. Isn't
it
being excreted as perchlorate? Ed or Dave, can you explain the
thermodynamic issues again?

Annie.

CC: RTPMAINHUB.INTERNET("drogers@aflsa.jag.af.mil")